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(Citation 2)

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Applicants: Hitachi Kasei Kogyo K.K., Tokyo, (JP)

Title: Flame-retardant epoxy resin composition

SPECIFICATION

1. Title of the Invention

Flame-retardant epoxy resin composition

2. Scope of Claims for Patent

1. A flame-retardant epoxy resin composition

containing epoxy resin, acid anhydride, a cure accelerator, a flame retardant, and a filler, wherein silica and hydrated alumina are used as the filler, the silica having a particle size distribution in which an average particle diameter is 10 to 15 μm and a cumulative weight (%) of particles equal to or smaller than 3 μm is lower than 15%, and the hydrated alumina having a particle size distribution in which an average particle diameter is 6 to 12 μm and a cumulative weight (%) of particles equal to or smaller than 3 μm is lower than 12%.

3. Detailed Description of the Invention

(Field of Industrial Application)

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The present invention relates to flame-retardant epoxy resin compositions and, in more detail, to a flame retardant epoxy resin composition with a property of impregnation between wound wires being significantly improved.

(Prior Art)

Conventionally, since an epoxy resin has excellent electric characteristics, mechanical characteristics, and crack resistance, and also is excellent in adhesion property for various types of material, epoxy resin has been often used for electrical insulation, particularly, for cast molding. In particular, for the purpose of insulation protection and improvement in a high-voltage property (arc resistance, tracking resistance), crack resistance, and fire retardancy, a flame-retardant epoxy resin composition is used for a process of insulating high-voltage components, that is, for impregnation and cast molding. For example, a composition with acid-anhydride cure epoxy resin that contains a large amount of filler and flame-retardant is used.

In order to meet the recent demands of improvement in performance and reliability of electronic components, such a flame-retardant epoxy resin composition, particularly the one for a flyback transformer for television, for example, is desired to be excellent in insulating performance and

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property of impregnation between high-voltage wound wires. However, the conventional flame-retardant epoxy resin composition has drawbacks such that the interior of very thin wound wires, for example, enamel wires having a diameter of 0.05 mm, cannot be sufficiently impregnated with resin, thereby causing corona to occur at the time of operation in some cases, leading to an interlayer short circuit.

On the other hand, as described above, by mixing a large amount of filler into epoxy resin, heat generation at the time of hardening is controlled, cure shrinkage at the time of hardening is reduced, further a coefficient of linear expansion is reduced, and still further crack resistance is improved.

However, in case of the conventional technique according to which the particle size distribution of the filler compounded is not adjusted, the filler is separated and settles when the flame-retardant epoxy resin composition is hardened, so that the filler is non-uniformly dispersed in the hardened product, as a result of which the content of the filler in the upper portion of the cast material and the content of said filler in the lower portion differ from each other, so that there arises the problem that, by heat cycle, cracks are caused in the portion having a low content of the filler. Further, in

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case a filler having a particle size distribution in which many fine particles exist is used in order to prevent the filler from settling, when the interiors of the very thin wires are impregnated with the resin, the fine particle component clogs the upper portion of the very thin wires, as a result of which the impregnation properties are lowered, this being a drawback.

(Problem that the Invention is to solve)

It is the object of the present invention to eliminate the above-mentioned drawbacks of the conventional technique and to provide a flame-retardant epoxy resin composition that is superior in the impregnation of the interiors of the windings with said resin, and in addition, the settling properties of the filler is improved.

(Means for the Solution of the Problem)

The present inventors made ardent examination and researches in order to achieve the above-mentioned object, as a result of which the inventors have come to find out the fact that, by the use, as the filler, of silica and hydrated alumina with a specific particle size distribution, the above-mentioned problem can be solved, thus reaching the creation of the present invention.

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The present invention relates to a flame-retardant epoxy resin composition containing epoxy resin, acid anhydride, a cure accelerator, a flame retardant, and a filler, wherein silica and hydrated alumina are used as the filler, the silica having a particle size distribution in which an average particle diameter is 10 to 15 μm and a cumulative weight (%) of particles equal to or smaller than 3 μm is lower than 15%, and the hydrated alumina having a particle size distribution in which an average particle diameter is 6 to 12 μm and a cumulative weight (%) of particles equal to or smaller than 3 μm is lower than 12%.

The epoxy resin for use in the present invention has at least one epoxy group in a molecule. Examples include: bisphenol A epoxy resin obtained from bisphenol A and epichlorhydrin; bisphenol F epoxy resin obtained from bisphenol F and epichlorhydrin; glycidyl ester of polycarboxylic acid, such as phthalic acid, tetrahydrophthalic acid, hexahydroxyphthalic acid, sebacic acid, and dodecanoic acid; glycidyl ether of polyvalent alcohol, such as 1,4-butanediol, 1,6-hexanediol, polyethylene glycol, polypropylene glycol, and trimethylolpropane; alicyclic epoxy resin, such as 3,4-epoxycyclohexylmethyl (3,4-epoxycyclohexane) carboxylate; and epoxides of liquid polybutadiene.

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Examples of acid anhydride for use in the present invention include: methyltetrahydrophthalic anhydride; methylhexahydrophthalic anhydride; phthalic anhydride; hexahydrophthalic anhydride; endomethylenetetrahydrophthalic anhydride; dodecenylsuccinic anhydride; octenylsuccinic anhydride; and polyazelaic polyanhydride. The amount of use of acid anhydride is preferably within a range of 0.6 to 1.3 equivalent per epoxy group included in epoxy resin.

Example of the cure accelerator for use in the present invention include: imidazole, such as 2-ethyl 4-methylimidazole, 1-cyanoethyl 4-methylimidazole, and 1-benzyl 2-ethylimidazole, and their derivatives; and tertiary amine, such as trisdimethylaminomethylphenol. The amount of use of the cure accelerator is not particularly limited, but is preferably within a range of 0.1 to 0.5 parts by weight percent per 100 parts by weight of acid anhydride.

Examples of the flame retardant for use in the present invention include: hexabromobenzene; tetrabromobisphenol A; decabromodiphenyloxide; tribromophenol; dibromophenyl glycidyl ether; dibromocresyl glycidyl ether; and dibromoisopropylphenyl glycidyl ether, each of which is used solely, or two or more of which are mixed for use. A combination of a halogenated organic compound and

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antimonous trioxide can also be used. As for the amount of use of the halogenated organic compound and antimonous trioxide, the amount of the halogenated organic compound is normally within a range of 10 to 50 parts by weight and, preferably, the amount of antimonous trioxide is within a range of 3 to 15 parts by weight, with respect to 100 parts by weight of epoxy resin. A weight ratio of the halogenated organic compound to antimonous trioxide is preferably 2 to 1 to 3 to 1.

As the filler for use in the present invention, silica, which can be reduce a coefficient of linear expansion and is effective in crack resistance and moisture resistance, and hydrated alumina, which is effective in flame retardancy, arc resistance, and tracking resistance, are used in a combined manner.

In the present invention, an average particle diameter is a particle diameter (μm) with a cumulative weight (%) being 50%.

Silica has a particle size distribution in which the average particle diameter is 10 to 15 μm and a cumulative weight (%) of particles equal to or smaller than 3 μm is lower than 15%. When silica has an average particle diameter smaller than 10 μm and its cumulative weight (%) of particles equal to or smaller than 3 μm is larger than 15%, fine particle components in the composition are

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increased, thereby decreasing impregnation property. Also, when the average particle diameter is larger than 15 μm , coarse particle components are increased, thereby increasing a settling property of a filler of a hardened material.

Hydrated alumina has a particle size distribution in which the average particle diameter is 6 to 12 μm and a cumulative weight (%) of particles equal to or smaller than 3 μm is lower than 12%. When hydrated alumina has an average particle diameter smaller than 6 μm and its cumulative weight (%) of particles equal to or smaller than 3 μm is larger than 12%, the impregnation property is decreased, similarly to silica. When the average particle diameter is larger than 12 μm , the settling property is increased, similarly to silica.

Although depending on flame retardancy, operability, impregnation property, electrical property, moisture resistance, crack resistance, etc., of the flame-retardant epoxy, the compounding amount of silica and hydrated alumina for composition, resin composition is 60 to 260 parts by weight with respect to 100 parts by weight of epoxy resin, preferably, 130 to 200 parts by weight in view of arc resistance, tracking resistance, flame retardancy, crack resistance, and viscosity.

The compounding ratio of silica and hydrated alumina is arbitrary. However, when the compounding ratio of silica increases, moisture resistance is improved, but flame retardancy is decreased, and when the compounding ratio of hydrated alumina increases, effects are produced in a manner reverse to the above. Therefore, the compounding ratio of silica and hydrated alumina is preferably silica:hydrated alumina=40:60 to 80:20 (weight %).

The flame-retardant epoxy resin composition according to the present invention can include, as required, a coloring agent, such as colcothar, hydrated ferric oxide, and carbon; a silane coupling agent, a titanium coupling agent; an silicone antiforming agent, a reactive epoxy diluent, etc.

(Effect of the Invention)

The flame-retardant epoxy resin composition according to the present invention is excellent in impregnation between wound wires, and also has an improved settling property of a filler.

The flame-retardant epoxy resin composition according to the present invention is excellent in arc resistance and tracking resistance, and also has a high flame retardancy of 94V-0 in a UL94 test.

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The flame-retardant epoxy resin composition according to the present invention can be widely used for impregnation and cast molding of flyback transformers, high-voltage transformers, power transformers, switching transformers, solenoid coils, and others.

(Examples)

Hereinafter, the present invention is described with reference to examples.

The term "parts" in the examples described below means parts by weight.

Here, the flame-retardant epoxy resin composition was hardened at 75 degrees Celsius for 2.5 hours and then at 110 degrees Celsius for 2.5 hours. Also, each property was measured through the following method.

(1) Particle size distribution of the filler: Using SediGraph 5000 ET manufactured by Shimadzu Corporation, preliminary distribution and ultrasonic cleaning were performed for 20 minutes with a sample concentration of approximately 8 weight %, a start particle diameter of 50 μm , and a fluid dispersion of hexametaphosphoric acid soda of 0.1 weight % to form a particle diameter distribution chart, thereby finding a cumulative weight % of the particle diameter.

An average particle diameter shown is of particles having a particle diameter (μm) with a cumulative weight (%) of 50%.

(2) Viscosity: Using a B-type rotating viscometer, measurement was performed at a measurement temperature of 25 degrees Celsius.

(3) Model settling property: The sample was cast in a polyethylene test tube of 18 mm ϕ to a height of 130 mm, and then hardened under the hardening conditions described above. Thereafter, a burnt residue of portions of 1 cm each at upper and lower ends of the hardened material were measured to find a difference between the upper and lower portions. A larger difference indicates a larger amount of settling of the filler in hardening.

(4) Model impregnation property: A polyethylene test tube of 15 mm ϕ was filled with glass beads having an average particle diameter of 60 μm to a height of 40 mm as being vibrated. Next, depressurized at 10 torr, the sample was injected to a height of 80 mm, and then was hardened under normal pressure with the hardening conditions described above. Then, a model impregnation ratio was calculated from the following equation.

$$\text{Model impregnation ratio (\%)} = (W_0 - W_1) / W_0 \times 100$$

W_0 : initial weight of glass beads (g)

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W_1 : weight of glass beads of a not-impregnated portion (g)

The model impregnation property is to find the amount of the sample with which glass beads are impregnated during hardening. A smaller amount of glass beads in a not-impregnated portion indicates an excellent impregnation property.

(5) Actual-device impregnation property: A model coil was formed by winding 250 urethane wires having a diameter of 0.05 mm ϕ around a bobbin (10 slits) made of denatured polyphenylene oxide, was put in a case made of the same material as that of the bobbin, and was then preheated at 110 degree for 1.5 hour. Then, depressurized at 5 torr, the sample at 35 degrees Celsius was injected for 30 seconds, and was then returned to normal pressure. Next, the sample was hardened under the hardening conditions described above, its center portion was cut and polished to observe the sample for a ratio of impregnation between wounded wires through a microscope. The impregnation ratio was calculated for each slit from the following equation.

$$\text{Impregnation ratio (\%)} = (1 - V/T) \times 100$$

T: the number of winding of the coil

V: the number of voids in the coil

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The average impregnation ratio is represented by an average value of impregnation ratios of all slits.

The actual-device impregnation property was evaluated with reference to the following criteria.

good: impregnation ratio over 99%

not-so-good: impregnation ratio of 97 to 99%

poor: impregnation ratio below 97%

(6) Arc resistance: Measured in accordance with JIS K 6911.

(7) Flame retardancy: Evaluated in accordance with UL 94 with a sample having a test strip thickness of 1.58 mm.

(8) Actual-device settling property: A model coil created in a manner similar to that for measuring the actual-device impregnation of (5) was cut from its center portion and polished, then separation and settling of the filler in the coil were observed through a microscope to evaluate the actual settling property with reference to the following criteria.

good: no separation or settling of the filler observed

not-so-good: slight separation and settling of the filler observed

poor: separation and settling of the filler observed

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First to fourth examples

Using the filler (silica and hydrated alumina) shown in Table 1, flame-retardant epoxy resin compositions having compositions shown in Table 2 according to the present invention (first to fourth examples) are formulated for evaluation of each property. The results are shown in Table 2. Numerics in composition are in parts by weight.

First to sixth comparison example

By using a filler (silica, hydrated alumina) shown in Table 1, epoxy compositions having compositions shown in Table 2 (first to sixth comparison examples) are formulated for evaluation of their properties. The results are shown in Table 2. Numerics in composition are in parts by weight.

(Table 1) (See the attached translation of the designations (Table 2) according to the reference numbers in said tables in the original publication.)

The model settling property of resin compositions of each of the first to fourth examples was small within a range of 0.5 to 1.0%. The filler of the actual device did not show separation or settling. Also, as for the model impregnation property, the composition was well impregnated within a range of 83 to 90%. Furthermore, the actual-device impregnation property was excellent with an

impregnation ratio over 99%. Still further, flame retardancy was 94V-0. Still further, the viscosity of the composition is low, thereby allowing an easy injection operation.

Silica used for the first comparison example (crystallite AA) has fine particles with its average particle diameter of 7.5 μm and a cumulative weight (%) of particles equal to or smaller than 3 μm is 15%. Similarly, hydrated alumina (C308) is a filler having an average particle diameter of 8 μm but a large cumulative weight (%) of particles equal to or smaller than 3 μm being 13%. As for the properties of the composition, its impregnation ratios are poor such that the model impregnation ratio is 68% and the actual-device impregnation ratio is not-so-good (97 to 99%).

Also, as with the first comparison example, the composition of the filler in the second example obtained by combining crystallite VX-3K and hydrated alumina (C308) has properties including poor impregnation ratios such that the model impregnation ratio is 71% and the actual-device impregnation ratio is not-so-good (97 to 99%), and are poorer than that in the first example in impregnation ratio.

In the third comparison example, as hydrated alumina, a filler is used having many fine particle components with an average particle diameter of 5 μm and a cumulative

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weight (%) of particles equal to or smaller than 3 μm being 30%. The properties of the composition are such that, even with a combined use of crystallite VX-3K, the model impregnation property is 55% and the actual-device impregnation property is no-so-good (97 to 99%). Therefore, the impregnation ratios are poor.

In the fourth comparison example, as silica, a filler is used having many fine particle components with an average particle diameter of 5.5 μm and a cumulative weight (%) of particles equal to or smaller than 3 μm being 25%. The properties of the composition are such that, even with a combined use of hydrated alumina C-308H, the model impregnation property is 42%, which is significantly low, and the actual-device impregnation property is poor (below 97%). Thus, the impregnation property is the poorest of all.

In the fifth comparison example, as silica, a filler is used having coarse particles with a cumulative weight (%) of particles equal to or smaller than 3 μm being below 15 but an average particle diameter of 9 μm . The properties of the composition are such that, even with a combined use of hydrated alumina C-308H, the model settling property is as large as 4.5%. Also, as for the actual-device settling property, separation and settling of the

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filler occur, therefore a crack may occur due to a heat cycle.

From the results shown in Table 2, the flame-retardant epoxy resin compositions of the examples are more than equivalent to and even excellent in comparison with the compositions of the comparison examples in settlement property of the filler at the time of hardening. Also, impregnation between wound wires is significantly improved.

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Table 1

101	FILLER
102	MANUFACTURER
103	PARTICLE SIZE DISTRIBUTION
104	AVERAGE PARTICLE DIAMETER (μm)
105	EQUAL TO OR SMALLER THAN 3 μm (CUMULATIVE WEIGHT %)
106	SILICA
107	HYDRATED ALUMINA
108	CRYSTALLITE AA
109	CRYSTALLITE A1
110	CRYSTALLITE CMC-12
111	CRYSTALLITE VX-3K
112	HYDRATED ALUMINA C-308
113	HIGILITE H32
114	HYDRATED ALUMINA C-308H
115	TATSUMORI LTD.
116	SUMITOMO CHEMICAL CO., LTD.
117	SHOWA LIGHTMETAL INDUSTRIES CO., LTD
118	SUMITOMO CHEMICAL CO., LTD.

Table 2

201	COMPOSITION NUMBER
202	EXAMPLE
203	COMPARISON EXAMPLES

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- 204 EPIKOTE 828
- 205 ANTIMONY TRIOXIDE
- 206 CRYSTALLITE AA
- 207 CRYSTALLITE A1
- 208 CRYSTALLITE CMC-12
- 209 CRYSTALLITE VX-3K
- 210 HYDRATED ALUMINA C-308
- 211 HIGILITE H32
- 212 HYDRATED ALUMINA C-308-H
- 213 SILANE COUPLER
- 214 2-ETHYL-4-METHYL IMIDAZOLE
- 215 VISCOSITY
- 216 MODEL SETTLING PROPERTY
- 217 ACTUAL-DEVICE SETTLING PROPERTY
- 218 MODEL IMPREGNATION PROPERTY
- 219 ACTUAL-DEVICE IMPREGNATION PROPERTY
- 220 ARC RESISTANCE
- 221 FLAME RETARDANCY
- 222 EQUAL TO OR LARGER THAN 120

(Notes)

- 1) Manufactured by Yuka-Shell Co., Ltd.
bisphenol A epoxy resin
- 2) Manufactured by Nagase Co., Ltd.
reactive epoxy diluent
- 3) Manufactured by Nippon Kayaku Co., Ltd.

brominated cresylglycidyl ether

- 4) Manufactured by Shouei Chemical Products Co., Ltd.

hexabromobenzene

- 5) Manufactured by Hitachi Chemical Co., Ltd.

methyltetrahydrophthalic anhydride

- 6) Manufactured by Shikoku Chemicals Corporation

Trade Name "Curezole 2E4M2"